GAMMA-INDUCED EFFECT ON THE LUMINESCENCE OF NANOCOMPOSITES OF MEH-PPV CONDUCTIVE POLYMER WITH LEAD SULPHIDE QUANTUM DOTS

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Gamma radiation effect on the photoluminescence of thin films of conductive polymer MEH-PPV, PbS quantum dots (QDs) and MEH-PPV−PbS (QDs) nanocomposite have been studied. Thin films were obtained by centrifugation. Samples were irradiated with exposure doses (in Gy): 0; $1.84 \cdot 10^4$; $4.18 \cdot 10^4$; $6.73 \cdot 10^4$. Photoluminescence of the polymer MEH-PPV was established to change nonmonotonically with an increase in doses, which might be due to running the oppositely directed, competing processes under the action of gamma quanta, namely destruction and cross-linking of polymer chains. Significant polymer's restructuring took place under gamma rays. Photoluminescence intensity of PbS QDs fell approximately twofold after irradiation with doses mentioned above, the intensity maximum shifting to the short-wavelength region. This behavior was due to a change in the energy structure of the QDs. The effect of gamma quanta on the QDs photoluminescence was analyzed.

Key words: conductive polymer; quantum dot; MEH-PPV; PbS; photoluminescence; gamma quantum

Introduction

Nanocomposites based on conductive polymers and semiconductor nanocrystals show promise for use in optoelectronic devices with flexible parameter settings [1].

Different combinations of conductive polymers and semiconductor nanoparticles (quantum dots (QDs)) make it possible to customize the optical properties of nanocomposites [2 − 4]. At the same time, varying the size of QDs of different materials allows to generate the required optical spectrum of the nanocomposite and its properties. The optical properties of nanocomposites can be further altered by exposure to ionizing radiation, in particular, gamma radiation. Gamma rays can affect both the material of the polymer matrix and the semiconductor nanoparticles. Due to the physical properties of gamma radiation, its penetrating power is strong. Interactions between gamma rays and matter include electronic excitation, electron ionization and electron-hole pair generation [5].

The effect of gamma-ray irradiation on CdS, CdSe/ZnS and $CsPbBr_3$ quantum dots was considered in [6 − 8], with analysis of possible degradation mechanisms. It was established in [6] that irradiation with gamma rays affected the sizes of the reverse micellar systems used to synthesize the QDs and of their aqueous cores, with the changes in size due to irradiation depending on the conditions in which the specific QDs were obtained. QDs were shown to decrease in size as a function of the level of micelle hydration and the irradiation dose. The authors concluded that γ-irradiation could change the size of CdS quantum dots and, as a consequence, consistently change their parameters and properties (intensity, lifetime, and fluorescence band position).

Ref. [7] considered the effect of gamma radiation from a ^{137}Cs source on the photoluminescence properties of colloidal CdSe/ZnS quantum dots. Optical degradation was estimated depending on the irradiation dose. The authors linked the decrease in the photoluminescence decay time constants with recombination of exciton states. At the same time, the deterioration in quantum efficiency was attributed to nonradiative processes that did not involve exciton states and consisted in the trapping of excited carriers by irradiation-induced defects. In general, these quantum dots

were found to exhibit poor radiation hardness.

Ref. [8] examined the effect of gamma radiation from a ^{137}Cs source on perovskite $CsPbBr_3$ QDs. It was revealed that $CsPbBr_3$ QDs were significantly more stable with respect to γ-radiation than commercial samples of CdSe/ZnS QDs traditionally used for the same tasks. The observed degradation processes were described assuming that a dose-dependent drop in photoluminescence was related not only to a change in the particle size distribution but also to the formation of nonradiative recombination centers as a result of the material's exposure to high energy. The authors proposed using $CsPbBr_3$ nanocrystals as potential *in vivo* biosensors under increased radiation background during antitumor therapy.

Some studies explored the effect of gamma irradiation on various polymers. Ref. [9] confirmed that it was possible to fabricate a thermally stable polymer by means of radiation cross-linking, with a modified polymer formed by cross-linking of short monomer units of the initial polymer. The study determined the threshold doses causing irreversible changes and the doses of complete oxidation of fragmented units, and described the changes in the fundamental physical and chemical properties of the polymers, such as the band gap value.

Ref. [10] studied the changes in the molecular weight of a polymer exposed to gamma irradiation that were induced by cross-linking (elongation) and degradation (shortening) of the main polymer chain depending on the irradiation dose. The findings of this paper were rather controversial, yet important. Both processes were shown to occur simultaneously, but with different probabilities. This complicates quantitative assessment and prediction of the final properties of the material. Notably, the technology of radiation cross-linking of polymers is currently used in industry for insulation of deep-water cables with the required performance characteristics, as well as for orthopedic applications [11].

In turn, the effect of gamma irradiation on polymer − QD nanocomposites is rather poorly understood at present and needs a more in-depth approach.

In this study, we have investigated for the first time the degradation of the photolumi- nescent properties of the MEH-PPV polymer nanocomposites with lead sulfide (PbS) quan- tum dots, exposed to gamma irradiation and the effect of this irradiation on PbS QDs.

Experimental procedure

The samples were prepared from the commercially available MEH-PPV (Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]) polymer powder from Sigma Aldrich with a number-average molecular weight of about 40,000 − 70,000. PbS QDs were synthesized by a method identical to that used in [4] from an organometallic solution based on lead oxide (PbO) dissolved in oleic acid ($C_{18}H_{34}O_2$). Bis-trimethylsilyl sulfide in trioctylphosphine was introduced into this solution.

We should note that Ref. [4] proved that it was possible to use these QDs to create a polymer-QD nanocomposite, and also considered the potential applications of nanocomposites.

In our study, a toluene solution was prepared to obtain thin films of the MEH-PPV polymer, the PbS QDs, and their composite. The solution was deposited on glass substrates by centrifugation (the spin-coating technology). It is known that centrifugation should not lead to noticeable destruction of macromolecules [12]. The spinner's parameters (rotation rate, acceleration, etc.) can be changed with high precision, so that thin films of a given thickness can be obtained.

The initial industrial MEH-PPV polymer powder (weight about 10 mg) was dissolved in toluene (the solution was immersed in an ultrasonic bath for 20 minutes to completely dissolve the polymer). The PbS QDs and the composite (MEH-PPV + PbS QD) were prepared in toluene. The glass substrates were pretreated in the ultrasonic bath filled with isopropyl alcohol for 10 minutes. The MEH-PPV and PbS QD films and their composites were deposited on glass substrates by spin-casting.

Photoluminescence of the samples was excited by a semiconductor laser with a wavelength $\lambda = 405$ nm and a power of 50 mW, operating in continuous mode. The photoluminescence spectra were recorded using the Horiba Jobin

Yvon automated system including a FHR 640 monochromator with a 1200 gr/mm diffraction grating and a Symphony II 1024*256 Cryogenic Open-Electrode CCD detector.

The gamma radiation source was a ^{137}Cs radionuclide with a photon energy of 661 keV. The samples were irradiated in a quasi-closed oxygen-containing chamber by a monochromatic gamma-ray flux, which was achieved by using 84 radiation sources. In our case, a cesium source of gamma rays (^{137}Cs) has a number of advantages compared with a cobalt source (^{60}Co), primarily a lower gamma energy and less penetrating power; this allows to generate more single interactions. In other words, other things being equal, the linear attenuation coefficient is higher for the cesium isotope than for the cobalt isotope.

The thin films we have examined were exposed to the following irradiation doses, Gy: 0; $1.84 \cdot 10^4$; $4.18 \cdot 10^4$; $6.73 \cdot 10^4$.

All irradiations and measurements were performed at room temperature.

Experimental results and discussion

The photoluminescence spectrum for the conductive polymer − QD nanocomposite contains both the luminescence spectrum of the conductive polymer and the luminescence spectrum of quantum dots, as well as their combined energy band diagram. Fig. 1 shows the luminescence spectra of the MEH-PPV polymer, PbS QDs and MEH-PPV − PbS QD films (deposited on a glass substrate), recorded after exposure to different doses of gamma radiation.

Irradiation of the pure MEH-PPV polymer with gamma rays results in various changes in polymer chains, which in turn changes the luminescence spectra. Gamma irradiation randomly breaks the C − C and C − H bonds, and also leads to oxidative degradation with different functional groups forming in the presence of oxygen [10].

Fig. 1, *a* shows the photoluminescence spectra of the gamma-irradiated MEH-PPV polymer. Evidently, the luminescence intensity decreases sharply at an irradiation dose of $1.84 \cdot 10^4$ Gy, and increases as the dose is further increased, with a subsequent slight decrease in intensity. Additionally, a broadening of
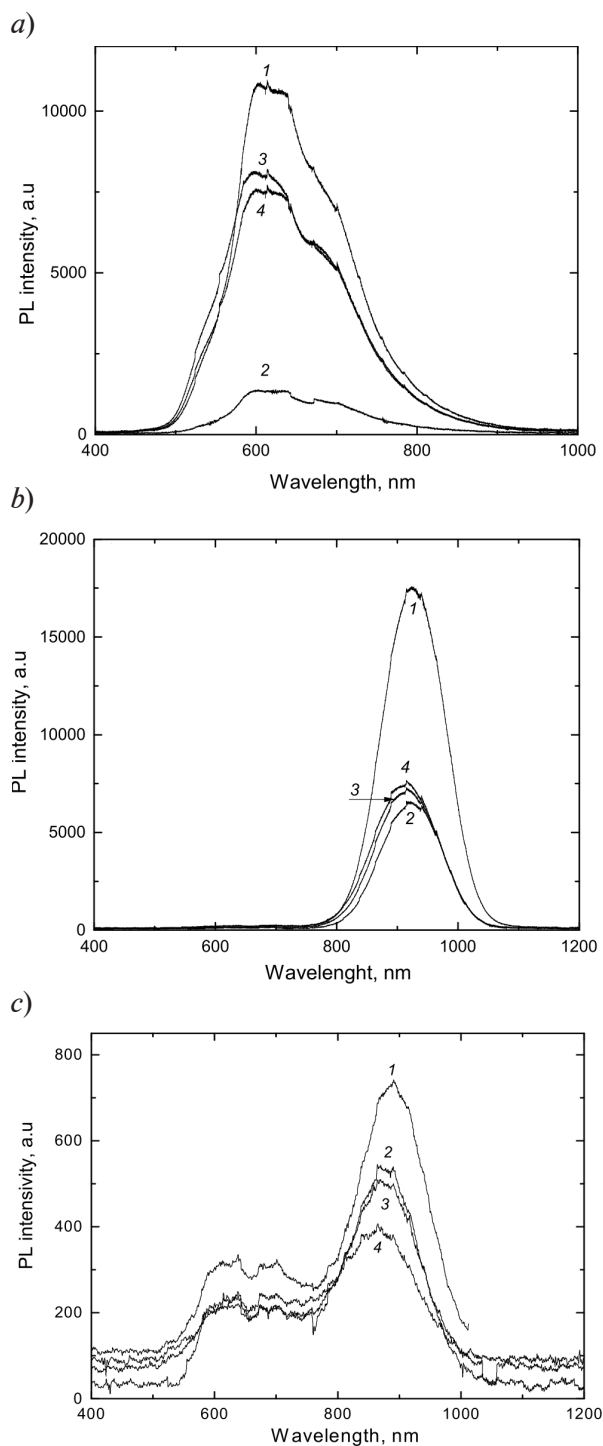

Fig. 1. Photoluminescence spectra for a pure MEH-PPV polymer (*a*), PbS QDs (*b*), and a MEH-PPV − PbS QD polymer nanocomposite (*c*), deposited on glass substrates; recorded after exposure to different doses of gamma irradiation, Gy: 0 (*1*); $1.84 \cdot 10^4$ (*2*); $4.18 \cdot 10^4$ (*3*); $6.73 \cdot 10^4$ (*4*)

the spectrum is observed with a shift in the intensity maximum toward short wavelengths and with an insignificant broadening toward long wavelengths at the doses of $4.18 \cdot 10^4$ and $6.73 \cdot 10^4$ Gy.

This behavior of the luminescence spectrum can be attributed to structural changes ocurring in the polymer. At low irradiation doses, the key role is played by cross-linking of polymer chains [9] that promotes the decay of the exciton excited during activation. Cross-linking facilitates the transition of an electron or a hole to an adjacent polymer chain with the corresponding exciton decay and subsequent nonradiative recombination. Besides, the arising defects contribute to the formation of nonradiative recombination centers, which electrons and holes reach rather quickly via long conjugated chain segments. A further increase in the irradiation dose leads to a shortening of the conjugated chain segments, which is manifested in the luminescence intensity maximum shifting toward short wavelengths. This also hinders the decay of excitons due to transition of electrons or holes to adjacent conjugated sites or adjacent polymer chains and to increased luminescence intensity. Since the transfer of electrons and holes from one conjugated site to another or to an adjacent chain occurs via a hopping mechanism, this process is hampered by an increase in the length distribution of the conjugated segments and a corresponding increase in the energy distribution [13]. Luminescence intensity increases as a result. The number of defects and, consequently, the number of nonradiative recombination centers increase with a further increase in the dose, and luminescence intensity gradually decreases.

Fig. 1, *b* shows the luminescence spectra of PbS QDs with different irradiation doses. With increasing irradiation dose, the luminescence peak shifts toward the shortwave region of the spectrum, and the peak width increases. The luminescence intensity decreases significantly with an irradiation dose of $1.84 \cdot 10^4$ Gy, and then increases slightly with an increase in the irradiation dose. This can be attributed to a whole range of processes occurring in colloidal QDs irradiated with gamma rays. Gamma irradiation can affect the size of the QDs [6].

Defects leading to an increase in nonradiative recombination can form within QDs. Defects similar to defects in polymer chains can occur in the organic molecules surrounding the QD. In combination with oxygen atoms, this process can lead to the formation of charge trapping centers. As a result, an electric charge is generated around the QD. Regardless of the sign of the charge, this leads to a shift in the quantum confinement subbands of the QD and an increase in the effective band gap, which in turn causes the luminescence peak to shift toward the short wavelengths. The broadening of the spectrum is due either to an increase in the size distribution of the QD, or in the distribution of the electric charge surrounding the QD.

Fig. 1, *c* shows the luminescence spectra of the MEH-PPV – PbS QD nanocomposite. The luminescence intensity of the polymer decreases substantially when the nanocomposite is formed, while the luminescence intensity of the QD remains rather high.

This effect is due to the specifics of the energy band diagram of the nanocomposite (Fig. 2). Electrons and holes excited in the polymer matrix are trapped into quantum dots and recombine with the emission of infrared rays. As a result, the luminescence intensity of the polymer matrix decreases, while that of the QD increases. Irradiation with gamma rays most significantly affects the luminescence intensity of the QD, which decreases with increasing irradiation dose, dropping by half compared to the unirradiated sample at a dose of $6.73 \cdot 10^4$ Gy. The luminescence intensity of the polymer matrix also decreases with an increasing dose of gamma irradiation but not so considerably as in the case of the QDs. A significant drop in the luminescence intensity of the QD is due not only to enhanced nonradiative recombination in the QD, but also to a change in the factors affecting the trapping of electrons and holes from the polymer matrix. The shift of the luminescence peak of the QD toward the short-wavelength region of the spectrum indicates a shift in the quantum confinement energy levels of the QD toward higher energies and a decrease in the depth of the quantum well for electrons and holes. This depth for holes can be reduced
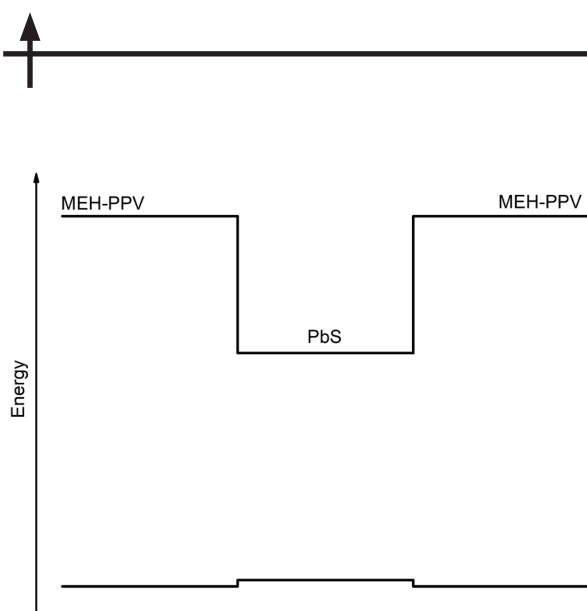
Fig. 2. Energy band structure
for the MEH-PPV – PbS QD nanocomposite

until it either becomes a very small value or the well disappears altogether.

Let us analyze the band diagram of the nanocomposite in Fig. 2 in more detail. A quantum well corresponding to the PbS QDs is located at its center, and the lines to the right and left of the well correspond to the LUMO and HOMO levels of the MEH-PPV polymer. Reducing the depth of the quantum well significantly reduces the probability of trapping and confinement of holes within the QD. The probability of trapping one of the types of carriers in the QD is also reduced due to the presence of an electric charge surrounding the QD. Due to these factors, the luminescence of the QD is considerably reduced. Decreased luminescence of the polymer matrix is due to both an increase in the number of defects and

an increase in the intersystem transition between the singlet and triplet exciton states in the polymer. The probability of this transition increases if heavy impurity atoms (with a large atomic number Z) are present in the polymer matrix [14]. These atoms, in particular, lead, can appear if the absorption of gamma rays by the quantum dot causes the release of such an atom from the QD into the polymer matrix.

Conclusion

Photoluminescence spectra of gamma-irradiated samples (the MEH-PPV – PbS QD nanocomposite and its components) were recorded and analyzed in this study. The following conclusions can be drawn based on our findings.

Gamma irradiation leads to a nonmonotonic decrease in the photoluminescence of the MEH-PPV polymer, which may be due to competing oppositely directed processes occurring in it, namely, degradation and cross-linking of polymer molecular chains. Significant structural changes occur in the polymer during these processes.

The photoluminescence of the PbS quantum dot irradiated with different doses in the range of $(1.84 - 6.73) \cdot 10^4$ Gy decreases approximately by half, with its intensity maximum shifting to the short-wavelength region; this points to a change in the energy structure of the QD.

The luminescence of a gamma-irradiated nanocomposite is determined by its energy band structure, which varies depending on the irradiation dose absorbed.

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